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# On the Influence of Ultra-violet Absorption on the Relative Intensities of Stokes and Anti-Stokes Lines in the Raman Spectrum.

By

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Plates III and IV.

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Abstract.

The value of $I_{AS}/I_S$ in the case of the 655 line due to $CS_2$ excited by the line 4358A has been determined experimentally, using blackening-log. intensity curves obtained with the help of a standardised tungsten ribbon lamp, for comparison of intensities. It has been found that the observed value of $I_{AS}/I_S$ definitely indicates the influence of absorption frequency on $I_{AS}/I_S$ and gives the value 1.776 for the factor

$$1+\frac{4\nu\,\nu_{mn}}{\nu_{jn}^2-\nu^2}$$

in the theoretical expression for $I_{AS}/I_S$ given by Placzek.

## 1. *Introduction.*

It has been reported by the author in a previous paper[1] that the experimental values of the ratio of the intensities of anti-Stokes and Stokes lines in the Raman spectrum due to carbon tetrachloride agree more closely with the expression

$$\left(\frac{\nu+\nu_{mn}}{\nu-\nu_{mn}}\right)^4 e^{-\frac{h\nu_{mn}}{KT}}$$

[1] S. C. Sirkar, Ind. J. Phys., 6, 295 (1931).

than with the Boltzmann factor alone. It was also pointed out there that the experimental results were in agreement with the theory put forward by Placzek.[2] The actual expression for $I_{As}/I_s$ given by Placzek, however, is

$$I_{As}/I_s = \left(\frac{\nu+\nu_{mn}}{\nu-\nu_{mn}}\right)^4 \left(1+\frac{4\nu\,\nu_{mn}}{\nu_{jn}^2-\nu^2}\right) e^{\frac{-h\nu_{mn}}{KT}} \quad \ldots (1)$$

where $\nu_{mn}$ is the frequency shift of the Raman line, $\nu$ the exciting frequency and $\nu_{jn}$ is the predominant ultra-violet absorption frequency of the liquid. While the expression (1) was quoted in the previous paper,[2] the factor

$$1+\frac{4\nu\,\nu_{mn}}{\nu_{jn}^2-\nu^2}$$

was tacitly omitted by the author and it was not explained through inadvertence, that as the experiment was carried out in the visible region of the spectrum with carbon tetrachloride as the scattering liquid, the said factor was very nearly equal to unity, and was therefore omitted. In fact, the influence of ultra-violet absorption frequency on the value of $I_{As}/I_s$ was looked for even at that time in case of Raman lines due to carbon tetrachloride excited by the mercury line 3125A, but it was observed that the exposed liquid showed appreciable absorption in this region and the coefficient of absorption being observed to be different for different wave-lengths, it was not possible to compute the value of $I_{As}/I_s$ very accurately. The results obtained in the case of Raman lines excited by 3125A were, therefore, not very accurate and only those obtained in the case of lines excited by 4358A were reported. As all liquids exhibit absorption for wave-lengths much longer than that of the actual ultra-violet absorption band, when exposed to strong light of frequency approaching

[2] G. Placzek, Z. f, Phys. 58, 585 (1929).

that of the absorption band, it was thought that the problem of investigating the influence of ultra-violet absorption frequency on the value of $I_{AS}/I_S$ was beset with a serious difficulty. Recently, however, while investigating the dispersion of polarisation of Raman lines, it was observed by the author that in the case of carbon disulphide the said difficulty could be easily surmounted by using a constant distillation apparatus. As no report about the experimental investigation of the problem in question came to the author's notice, the present investigation was undertaken.

## 2. *Experimental.*

Since $\nu_{mn}$ appears in the exponential factor in the expression for $I_{AS}/I_S$, liquids having large values of $\nu_{mn}$ are not suitable for the present investigation, because, for large value of $\nu_{mn}$ the anti-Stokes line becomes so feeble that its intensity cannot be compared accurately with that of the Stokes line. Carbon disulphide, however, has got a strong 655 line and for this value of $\nu_{mn}$ the value of $I_{AS}/I_S$ is not too small to be determined accurately. Also this liquid has got absorption in the near ultra-violet and therefore was chosen for the present investigation.[3] In a preliminary experiment, the liquid was at first distilled in a Wood's tube and the spectrogram obtained with a Fuess glass spectrograph using a Zeiss step weakener as described in the previous paper[4] showed that the anti-Stokes line excited by the mercury line 4358A was much feebler in comparison with the Stokes line than indicated by the theory, even neglecting the influence of absorption frequency on $I_{AS}/I_S$. On measuring the absorption coefficient of the exposed liquid for different wavelengths in the method

[3] The author's thanks are due to Dr. G. Placzek who suggested in a private letter that $CS_2$ should exhibit the influence of absorption frequency on $I_{AS}/I_S$ according to his theory even in the visible region of the spectrum.

[4] S. C. Sirkar, *loc. cit.*

described in a previous paper[5] it was found that there was fairly strong absorption in the region of the anti-Stokes line excited by 4358A. This explained the feebleness of the anti-Stokes line observed in the preliminary experiments mentioned above. It was observed later on that when carbon disulphide was distilled in a constant distillation apparatus first used by Pal and Sen Gupta,[6] the 655 anti-Stokes line excited by 4358A was unexpectedly strong in a spectrogram obtained on an Ilford Golden Isozenith plate. The constant distillation apparatus was therefore used in the present investigation with a little modification. As the temperature of the scattering liquid appears in the exponential function in the expression for $I_{As}/I_s$, it was to be kept constant and measured as accurately as possible. In order to keep the temperature constant, the Wood's tube of the constant distillation apparatus was surrounded by a water jacket $J_2$ as shown in Fig. 1 and water from a small metal vessel placed in the room was made to

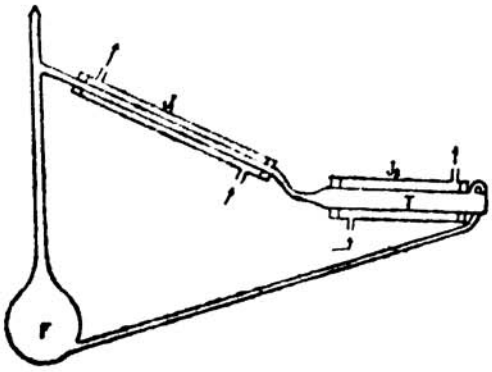


FIG. 1.

circulate constantly through the jacket with the help of a pump attached to the vessel and driven by motor. The ex-

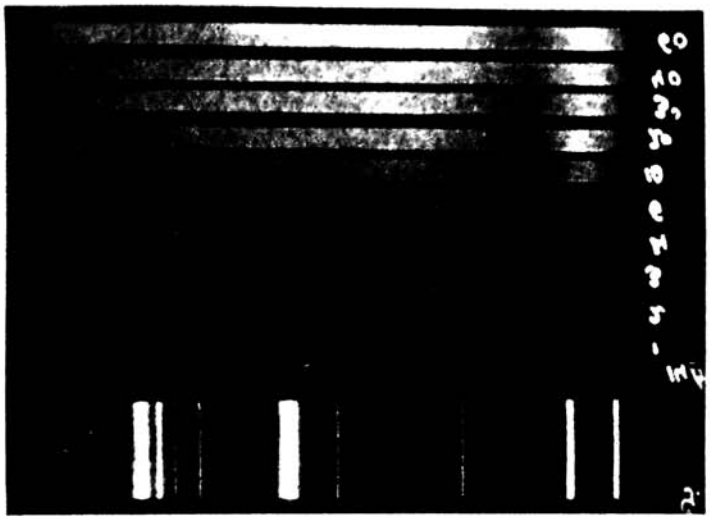
[5] S. C. Sirkar, Ind. J. Phys., 6, 138 (1931).
[6] N. N. Pal and P. N. Sen Gupta, Ind. J. Phys., 5, 609 (1930).

periment was carried in a corner of a room surrounded on three sides by big rooms and on the remaining side there was a three storied house at a distance of a few feet from it. On keeping all the doors of the said room closed and starting the mercury lamp, it was observed that the temperature of the room attained a steady state in about two hours and remained constant within 0·1°C throughout the day and night. The water circulating through the jacket $J_1$ was supplied by the tank on the terrace of the house. Kahlbaum's fresh carbon disulphide was introduced in the flask F and air was completely drawn out with a pump before the flask was sealed up. The liquid in the flask began to boil briskly on raising its temperature by a few degrees above room temperature with an electric heater. The temperature of the water circulating through the Jacket $J_2$ was measured frequently during the exposure with a 'Celsius' 1/10°C. 'Normal Glass' thermometer.

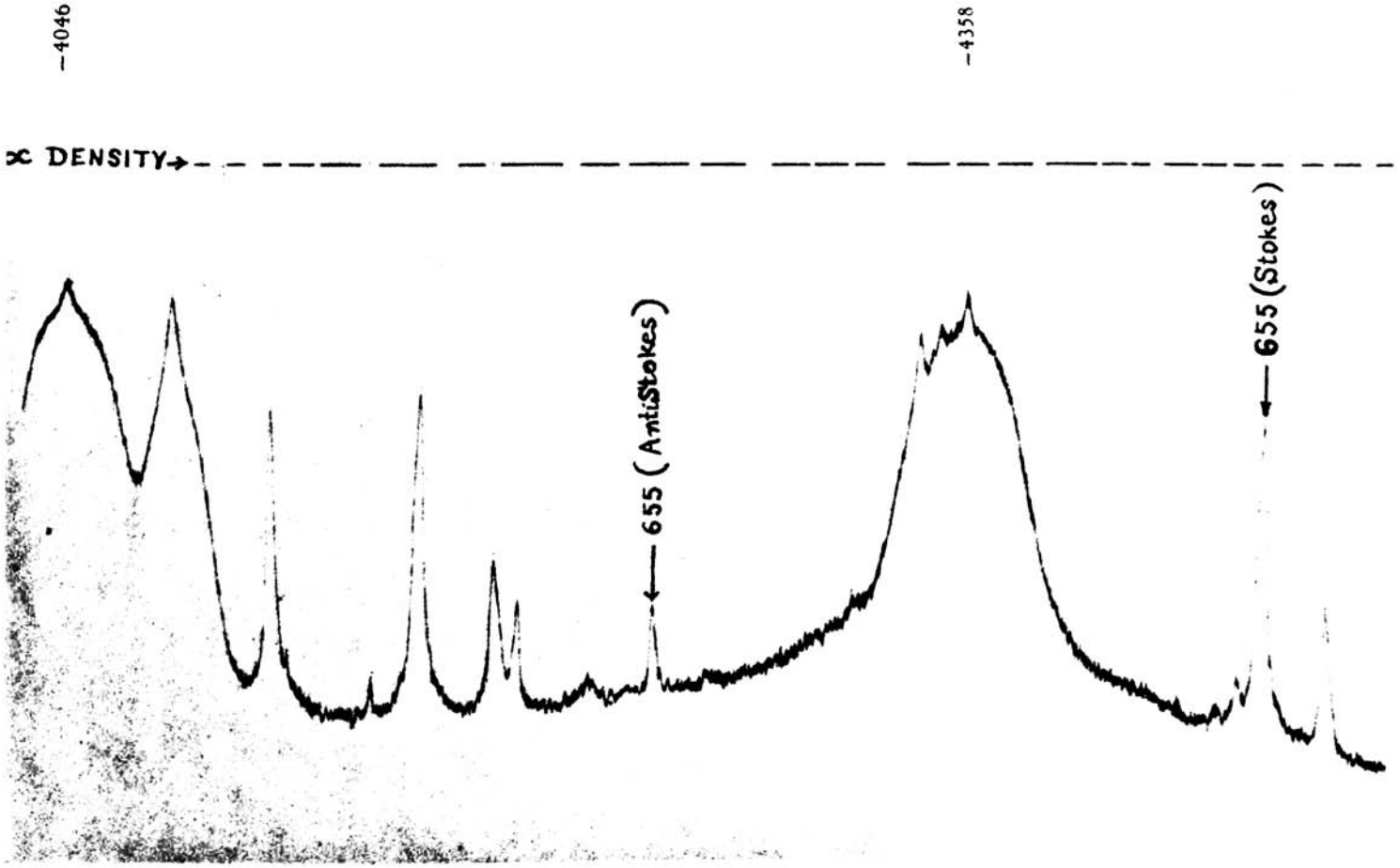
As the temperature of the water in jacket $J_2$ would be altered if the mercury lamp were placed near the Wood's tube, a big glass condenser was used to focuss the image of a Cooper Hewittic flat type mercury lamp on the Wood's tube T and the Raman spectrum was photographed on an Ilford Golden Isozenith plate using a Fuess glass spectrograph having a dispersion of about 20 A/mm in the region of 4358 A. On adjacent parts of the same plate, intensity marks were taken by varying the width of the slit of the spectrograph and using a strip of unglazed white paper illuminated by a standardised tungsten ribbon lamp as source of light. The current through the lamp was measured with a good Weston ammeter. The slit of the spectrograph was calibrated with a travelling microscope. The mercury line 4358A was also recorded feebly on each of the intensity marks in order to find accurately the positions of the Stokes and anti-Stokes lines on the intensity marks due to continuous spectrum. The exposure for each intensity mark was two

minutes and for the Raman spectrum about 20 hours. A Moll's self registering microphotometer was used to measure the densities of the intensity marks and of the Raman lines. As the densities of the lines on the plate were not very uniform throughout the lengths of the lines, great care was taken to measure the densities of the Stokes and anti-Stokes lines at corresponding points in their lengths. The plate was first adjusted carefully so that on moving it by turning the shaft, the spot of light focussed on the lines appeared to pass through corresponding parts of the lengths of all the lines in the spectrogram, and then the microphotometric record for the whole spectrum was taken. Deflections for the background of the plate on both sides of each of the intensity marks were noted. The blackening-log intensity curves were then drawn for the wavelengths of the 655 Stokes and anti-Stokes lines excited by 4358 A. The intensity corresponding to the slit width of ten divisions was plotted as 100 for both the wavelengths and with the help of the blackening-log intensity curves thus obtained, the intensity of the Stokes lines was compared with that of the corresponding wavelength in the standard continuous spectrum and that of the anti-Stokes line also was similarly compared with that of the corresponding wave-length in the standard spectrum. The true relative intensities of these two wavelengths in the standard continuous spectrum were then calculated from Wien's law. The true and colour temperatures of the tungsten ribbon lamp for different currents were given in a calibration chart kindly supplied by the manufacturers, Philips Lamp Works, Eindhoven. The true temperature was used in the calculations in the present case and values of emissivities were taken from those given by Hulbert.[1] The blackening log-intensity curves for the wavelengths 4486 A and 4237 A are reproduced in Fig 2.

[1] E. O. Hulbert, Astrophys. J., 45, 149 (1917).




Raman spectrum of carbon disulphide.




Microphotometric record of Raman spectrum of carbon disulphide.

### 3. *Results and Discussion.*

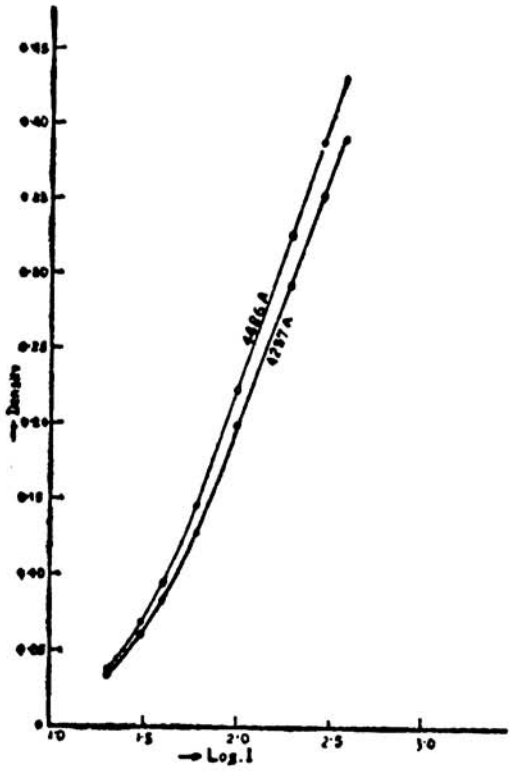



FIG. 2.

The spectrogram and the microphotometric records are reproduced in Plates III and IV respectively. The densities of the Raman lines of wave-lengths 4486 A and 4237 A obtained from the microphotometric record reproduced in Plate IV are 0·33 and 0·079 respectively. The blackening intensity curves for the wavelengths 4486 A and 4237 A in the continuous spectrum, as shown in Fig. 2 are drawn in such a way that in each case the intensity due to the width of the slit equal to ten scale divisions is taken as 100. On examining Fig. 2, it will be found that if $I_1$ and $I_2$ be the absolute

intensities of the wave lengths 4486 A and 4237 A in the continuous spectrum respectively, compared to $I_1$, the value of $I_S = 208$ and compared to $I_2$, the value of $I_{AS}$ is 36.

Therefore

$$\frac{I_{AS}}{I_S} = \frac{36}{208} \times \frac{I_2}{I_1}$$

In drawing the curves shown in Fig. 2, $I_2$ has been assumed to be equal to $I_1$, but actually it is not so. On applying Wien's law, taking $C_2 = 1 \cdot 432$, the actual value of $I_2/I_1$ is found to be $1 \cdot 264/2 \cdot 221$.

Hence

$$\frac{I_{AS}}{I_S} = \frac{36}{208} \times \frac{1 \cdot 264}{2 \cdot 221} = 0 \cdot 0984.$$

The temperature of the water, flowing through the jacket surrounding the tube containing the liquid was $27 \cdot 7°C$. The Boltzmann factor $e^{\frac{-h\nu_{mn}}{KT}}$ alone, for this temperature, would be $0 \cdot 0440$. The factor $\left(\frac{\nu + \nu_{mn}}{\nu - \nu_{mn}}\right)^4$ in this case is $1 \cdot 258$, so that without considering the factor containing ultraviolet absorption frequency the value of $I_{AS}/I_S$ expected in this case is $0 \cdot 0554$. Since the observed value is nearly double this, the influence of absorption frequency in this case is definitely established.

An attempt may be made here to find the ultraviolet absorption frequency $\nu_{jn}$ from the Placzek's theory with the observed value of $I_{AS}/I_S$. Substituting the value of $I_{AS}/I_S$ in the expression (1) quoted in the present paper, we get

$$\frac{0 \cdot 0984}{0 \cdot 0554} - 1 = \frac{4\nu\nu_{mn}}{\nu_{jn}^2 - \nu^2}$$

or

$$\nu_{jn}^2 = 5 \cdot 15 \times \nu\nu_{mn} + \nu^2$$

Substituting the value of $\nu$ corresponding to wavelength 4358 A the value of $\nu_{jk}$ is about 24620 $cm^{-1}$. The corresponding wavelength is about 4060 A. This wavelength is slightly greater than that of the middle of the nearest absorption band, which as given in the Tables by Landolt and Bornstein [8], is about 3850 A.

The author's heartfelt thanks are due to Prof. Sir C. V. Raman, F.R.S. for his kind interest in the work.

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[8] Landolt Bornstein, Phys. Chem. Tables, 5 Auf., p. 459 (1927).